

Radiation in Explosions of Hydrogen and Air.

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In the first part of this paper the results of experiments are recorded on the emission of radiation during explosion and subsequent cooling of inflammable mixtures of hydrogen and air contained in a closed vessel; and in the second part of the paper some experiments bearing on the transparency of the hot gaseous mixtures after explosion are described.

The results of a similar investigation in connection with inflammable mixtures of coal-gas and air have already been published.* The laws governing the emission of radiation in the hydrogen mixtures would appear to be similar in many ways to those governing the emission in the coal-gas mixtures; but in one or two respects there are important differences, which are of considerable interest in their bearing upon gaseous combustion.

Method of Experiment.

Full details of the experimental methods and apparatus employed have been given in the paper recording the results of the coal-gas and air experiments, but it will be convenient to describe them here very briefly. The inflammable mixtures were exploded in a cylindrical cast-iron vessel, 30 cm. in diameter and 30 cm. in length (see fig. 1). The pressure of the gaseous mixtures during explosion and subsequent cooling was measured by means of a Hopkinson optical indicator, which threw a spot of light on to a revolving photographic film. The radiation was measured by means of a platinum bolometer connected with a reflecting galvanometer, which also threw a spot of light on to the same revolving film. The bolometer was protected from the hot gaseous mixtures by means of a plate of fluorite, as shown in fig. 1. The fluorite transmits almost exactly 95 per cent. of radiation of the wave-length emitted by exploded hydrogen and air mixtures. After making an allowance of 5 per cent. for the absorption of the fluorite and 5 per cent. for reflection from the blackened surface of the bolometer, it is considered that the measurements from the films give radiation values of a high degree of accuracy.

The radiation emitted was measured in three positions on one of the end-covers of the explosion vessel, viz., at the top (position A, fig. 1), at the bottom (position B), and at the centre (position C).

* 'Phil. Trans.,' A, vol. 211, pp. 375-410.

When the bolometer was placed close up to the fluorite window, the radiation it received per square centimetre of its surface was equal to that received by a square centimetre of wall surface in the immediate neighbourhood; and when the bolometer was placed some distance away from the fluorite windows, the radiation it received came from a cone of the gaseous mixture of small solid angle (N , as shown in fig. 1). The experiments described in the first part of the paper were all made with the bolometer placed close to the fluorite window. Those described in the second part of the paper were made with the bolometer placed some distance behind the window. The measurements with the bolometer in this latter position have been divided

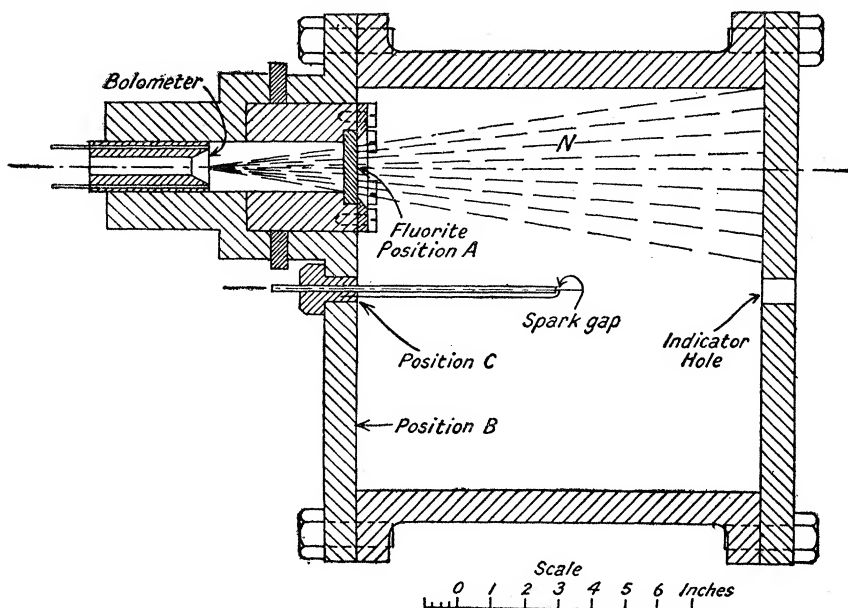


FIG. 1.

by the solid angle of the cone, so as to give the radiation from a cone of unit solid angle; and, following Prof. Callendar, this has been called the *intrinsic radiance*.

The hydrogen used in these experiments was supplied by the British Oxygen Company, guaranteed 98 per cent. pure.

PART I.—TOTAL RADIATION MEASUREMENTS.

Hydrogen and Air Mixtures of various Strengths.

The curves in fig. 2 relate to 25.4 per cent., 15.3 per cent., and 10.0 per cent. mixtures of hydrogen and air. Curves A_T , B_T , and C_T are the mean gas

temperature curves for these mixtures respectively. These have been calculated from the pressure records by means of the equation $pv = R\theta$, after making an allowance for the large contraction of volume which occurs during combustion. The radiation curves for the various mixtures, A_R , B_R , and C_R are the means of those measured in positions A, B, and C (see fig. 1),* and give, it is thought, a fairly reliable estimate of the mean radiation over the whole of the vessel walls. The dotted curves A_R' , B_R' , and C_R' are the differentials of the mean radiation curves and give the mean rate at which the walls of the vessel receive radiation per square centimetre per second at various times after ignition.

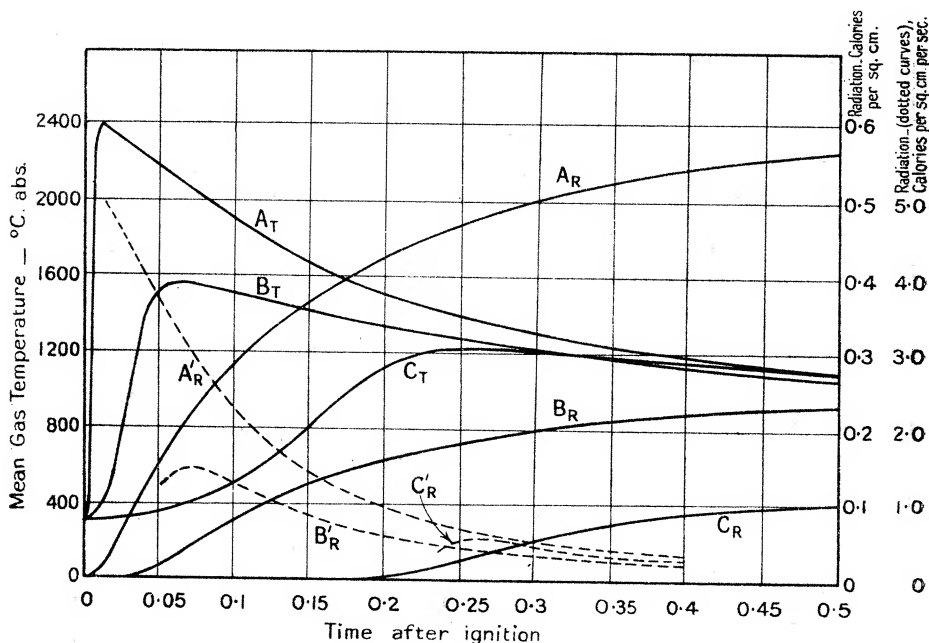


FIG. 2.

Tables I, II, and III have been prepared from the gas temperature and radiation curves in this figure. They show the mean radiation received by

* The rate at which radiation is received by the walls is from 10 to 20 per cent. greater in position C than in the other positions. The radiation curve for the 10 per cent. mixture has been calculated from a film record giving the emission from a cone of small solid angle of the gaseous mixture, which is proportional to the total radiation measured when the bolometer is placed close up to the plate of fluorite. This curve may not compare as regards accuracy with the curves for other mixture strengths both for this reason, and also because one record only was taken; but it is, I believe, substantially correct. All the experiments in the first part of this paper were made with the walls of the explosion vessel covered with a thin layer of dull black paint, so as to absorb all the radiation falling upon them.

Table I.—25·4 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 16,320 calories.

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·017	2400 (max. temp.)	0·018	0·5
0·05	2200	0·15	4·0
0·1	1920	0·285	7·7
0·15	1700	0·37	10·0
0·2	1530	0·425	11·4
0·25	1400	0·47	12·6
0·5	1100	0·57	15·5
0·75	910	0·59	15·8
1·0	810	0·60	16·1

Table II.—15·3 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 9700 calories.

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·065	1580 (max. temp.)	0·03	1·3
0·1	1510	0·085	3·8
0·15	1410	0·13	5·9
0·2	1340	0·16	7·2
0·25	1280	0·18	8·2
0·5	1080	0·23	10·3
0·75	900	0·24	10·8
1·0	810	0·245	11·0

Table III.—10·0 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 6450 calories.

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·24	1230 (max. temp.)	0·02	1·4
0·25	1220	0·03	2·0
0·3	1200	0·055	3·7
0·35	1180	0·075	5·1
0·4	1150	0·085	5·7
0·45	1120	0·095	6·4
0·5	1100	0·105	7·1
1·0	850	0·12	8·2

the walls per square centimetre and the proportion of the heat of combustion lost by radiation at various times after ignition. Table IV, which has been compiled from these tables, shows the total radiation received by the walls per square centimetre and the proportion of the heat of combustion lost by radiation during explosion and subsequent cooling in the various mixtures. Similar information in regard to coal-gas mixtures has been added for purposes of comparison.

It will be seen from the figures in Table IV that the proportion of the heat of combustion radiated off during explosion and subsequent cooling in the hydrogen mixtures varies greatly with the mixture strength, whereas in the coal-gas mixtures the variation in this proportion is small. Experiments on the analysis of the radiation emitted, which will be described presently, offer an explanation of these results.

It has been shown* that the total radiation emitted in coal-gas mixtures in the experimental vessel is a linear function of the maximum temperature developed. This relation is expressed by the equation

$$R_T = 0.00056 (\theta_{\max.} - 700),$$

where R_T is the total radiation received by the walls per square centimetre of surface, and $\theta_{\max.}$ is the maximum absolute temperature developed. A similar relation for the hydrogen mixture, based upon the three sets of figures in Table IV, is

$$R_T = 0.00042 (\theta_{\max.} - 950).$$

This equation, it is believed, may be relied upon to give reliable values of R_T for all hydrogen and air mixtures, at atmospheric density, within the limits of mixture strength 10 per cent. to 25 per cent., when exploded in a cylindrical vessel 30 cm. in diameter and 30 cm. in length, whose walls are blackened.

Table V has also been compiled from the figures in Tables I, II, and III. It shows the proportion of the heat of combustion lost by radiation up to the moment of maximum pressure in the hydrogen mixtures. Figures relating to coal-gas mixtures have been added for purposes of comparison.

It will be seen that, in the case of the coal-gas mixtures, the proportion of the heat of combustion radiated off during the explosion period increases very considerably as the mixture strength becomes weaker—a result which must be explained in terms of the increasing time of explosion, for the temperatures developed are, of course, lower in the weaker mixtures. In the case of the hydrogen mixtures, however, the increase in this proportion, as the mixture strength decreases, is not marked, even though in the weakest

* 'Phil. Mag.,' January, p. 81 (1920).

Table IV.

Hydrogen Mixtures.				Coal-gas Mixtures.			
Percentage strength of mixture.	Maximum temperature developed ($\theta_{\max.}$).	Total radiation received by walls per sq. cm. (R_T).	Total loss of heat by radiation per cent. heat of combustion.	Percentage strength of mixture.	Maximum temperature developed. ($\theta_{\max.}$).	Total radiation received by walls per sq. cm. (R_T).	Total loss of heat by radiation per cent. heat of combustion.
25.4	2400	0.60	16.1	15.0	2410	0.98	26.1
15.3	1580	0.245	11.0	13.0	2170	0.81	25.0
10.0	1230	0.12	8.2	9.8	1700	0.57	23.6

Table V.

Hydrogen Mixtures.				Coal-gas Mixtures.			
Percentage strength of mixture.	Time of explosion (secs.).	Maximum temperature developed ($^{\circ}$ C. abs.).	Percentage heat of combustion lost by radiation up to maximum pressure.	Percentage strength of mixture.	Time of explosion (secs.).	Maximum temperature developed. ($^{\circ}$ C. abs.).	Percentage heat of combustion lost by radiation up to maximum pressure.
25.4	0.017	2400	0.5	15.0	0.05	2410	3.3
15.3	0.065	1580	1.3	13.0	0.07	2170	3.7
10.0	0.24	1230	1.4	9.8	0.18	1700	7.0

mixture the time of explosion is as much as 0.24 second. The difference in the behaviour of the hydrogen and the coal-gas mixtures in this respect is interesting, and will be discussed presently in connection with later experiments.

The curves in fig. 3 have been prepared from the dotted curves in fig. 2. They show the rate at which the walls receive radiation per square centimetre per second during the cooling of the various hydrogen mixtures after explosion. The figures in Table VI have been compiled from the curves in

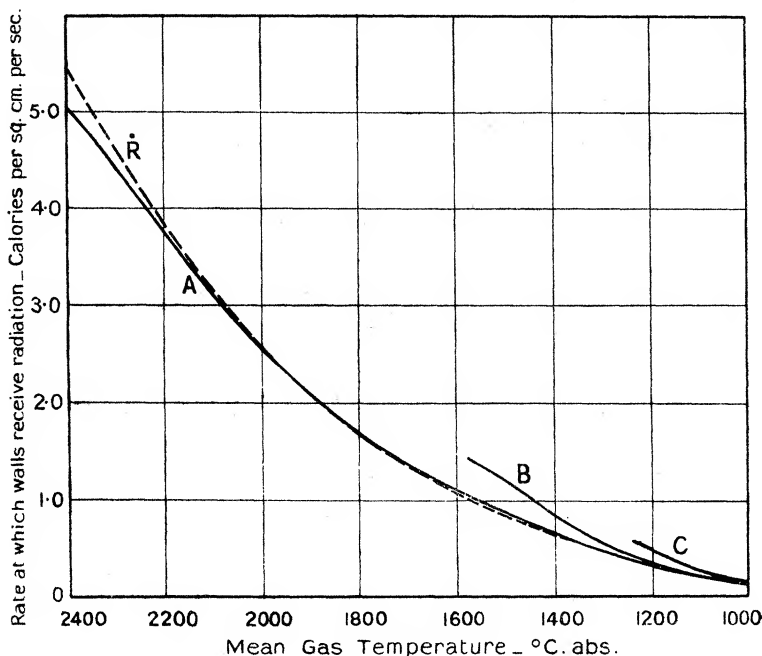


FIG. 3.

Curve A.—25.4 per cent. mixture of hydrogen and air.

„ B.—15.3 „ „ „

„ C.—10.0 „ „ „

„ $\dot{R} = 1.65 \times 10^{-14} \theta^4$.

this figure, and similar information has been added for coal-gas mixtures. This table shows that the hydrogen mixtures emit radiation at approximately the same rate as the coal-gas mixtures. They also show that the weak hydrogen mixtures, like the weak coal-gas mixtures, radiate more powerfully in the initial stages of cooling than the strong mixtures when they have cooled to the temperatures which the weak mixtures have in this epoch.

Table VI.

Mean gas temperature (° C. abs.).	Rate at which walls of vessel receive radiation, calories per sq. cm. per sec.					
	Hydrogen Mixtures.			Coal-gas Mixtures.		
	25·4 per cent.	15·3 per cent.	10·0 per cent.	15·0 per cent.	13·0 per cent.	9·8 per cent.
2400	5·0	—	—	5·4	—	—
2200	3·8	—	—	3·9	—	—
2170	—	—	—	3·7	4·0	—
2000	2·55	—	—	2·7	2·9	—
1800	1·7	—	—	1·8	1·8	—
1700	—	—	—	1·45	1·45	1·8
1600	1·1	—	—	1·15	1·15	1·2
1580	1·08	1·45	—	—	—	—
1400	0·7	0·85	—	0·65	0·65	0·65
1230	0·4	0·4	0·6	—	—	—
1200	0·35	0·35	0·5	0·3	0·3	0·3
1000	0·15	0·15	0·2	0·15	0·15	0·15

It has been shown* that the rate at which the walls receive radiation per square centimetre per second ($\dot{R}$) may, in the case of the coal-gas and air mixtures at atmospheric density, be estimated approximately by means of the equation

$$\dot{R} = 1.75 \times 10^{-14} \theta^4,$$

where $\dot{R}$ is expressed in calories per square centimetre per second and θ in degrees C. absolute. A very similar equation answers approximately in the case of the strong hydrogen mixtures. The equation to the dotted curve in fig. 3 is

$$\dot{R} = 1.65 \times 10^{-14} \theta^4.$$

Perhaps the most noticeable difference between radiation phenomena in hydrogen mixtures and those in coal-gas mixtures, as revealed by these experiments, is that, in the latter mixtures, the maximum rate at which radiation is emitted occurs during the explosion period,† when chemical activity is proceeding with great violence, while, in the hydrogen mixtures, it occurs at the moment of attainment of maximum temperature (or, indeed, perhaps a little later), when chemical activity has presumably in a large measure ceased. This is clearly shown by the dotted curves B_R' and C_R' (fig. 2),

* 'Phil. Mag.,' January, p. 79 (1920).

† The maximum rate of emission in the coal-gas mixture occurs near the time when the pressure curves undergo their second inflexion. See 'Phil. Mag.,' January, p. 70 (1920), and 'Phil. Trans.,' A, vol. 211, p. 381.

which give the rates of emission of radiation in the 15·3 per cent. and the 10·0 per cent. hydrogen mixtures respectively.

A quite different result was obtained in the case of the coal-gas mixtures when the bolometer was protected by windows of quartz and plate glass, which transmit for the most part radiation from steam, and cut off the bulk of that emitted by carbon dioxide. Records taken in this way show that the maximum rate of emission occurs near the second point of inflexion of the gas temperature curve during the explosion period—that is, at the same point as records taken with a fluorite window (which transmits radiation from both carbon dioxide and steam), show their maximum value.

Analysis of the Radiation Emitted in Hydrogen and Air Mixtures.

The infra-red spectrum of a hydrogen flame consists mainly of a well defined band, whose maximum is approximately at $2\cdot8\mu$, and there is little doubt that this band would be prominent in the spectrum of an exploded hydrogen mixture, though it may be somewhat broader than that of the naked flame, owing to the exploded mixture being at a higher pressure.* Radiation of other wave-lengths, however, would appear to be emitted in exploded hydrogen mixtures, as will be seen from the following experiments.

Table VII has been prepared from experiments made on 25·4 per cent. mixtures, first, when the bolometer was protected by the fluorite plate, and, secondly, when the fluorite plate was replaced by a plate of quartz.

Table VII.—Rate at which Radiation is received from 25·4 per cent. Mixtures of Hydrogen and Air per sq. cm. per sec. through Plates of Fluorite and Quartz. Bolometer in Position A.

Time from ignition (secs.).	Mean gas temperature. (° C. abs.).	Fluorite.	Quartz.	$\frac{\text{Quartz}}{\text{Fluorite}}$.
0·017	2400	4·7	3·65	0·79
0·045	2200	3·5	2·6	0·74
0·07	2000	2·45	1·65	0·67
0·12	1800	1·7	1·0	0·59
0·175	1600	1·1	0·6	0·55
0·25	1400	0·7	0·3	0·43
0·38	1200	0·35	0·1	0·29
0·60	1000	0·15	Nearly zero	Nearly zero

The quartz plate transmits about 70 per cent. of the radiation of wave-lengths between 2μ and $3\cdot5\mu$. It is more transparent than this to radiation

* Schaefer ('Ann. der Phys.,' vol. 16, I., p. 93) found that the *absorption bands* of CO_2 broadened as the pressure of the absorbing gas was increased.

of shorter wave-length than 2μ , and is opaque to radiation of greater wave-length than 3.5μ . The fluorite plate transmits almost exactly 95 per cent. of radiation over a very wide range of the infra-red spectrum (down to about 11μ). The radiation measurements through the fluorite plate have been corrected to the extent of 5 per cent. for this absorption, and if the emission spectrum of the hydrogen mixtures consisted simply of the 2.8μ band throughout cooling, it would have been expected that the ratio of the rate of emission through quartz to that through fluorite would have been fairly constant at about 0.7 for all gas temperatures.

This, however, was not found to be the case, as may be seen from Table VII. The ratio of the emission through quartz to that through fluorite decreases as the temperature decreases, indicating that there must be emitted by this mixture some radiation of greater wave-length than 3.5μ , which becomes of increasing importance relatively to the 2.8μ radiation as the temperature decreases.

At 1200°C. abs. the ratio is only 0.29, and at 1000°C. abs. it is practically zero. From these figures, it must be inferred that, in the neighbourhood of 1200°C. abs. , the 2.8μ radiation is rapidly ceasing to be emitted, and that, when the gas temperature has fallen to 1000°C. abs. , it has practically ceased, whereas, at these temperatures, radiation of greater wave-length continues to be emitted in appreciable quantities.

In the neighbourhood of the maximum temperature (2400°C. abs. to 2200°C. abs.), the ratio of the emission through quartz to that through fluorite is a little greater than 0.7. After making an allowance of 30 per cent. for the absorption of quartz, the radiation registered through quartz would thus appear to be greater than that registered through fluorite. A probable explanation of this is that in this epoch there is considerable energy in radiation of shorter wave-length than 2.8μ , for which the absorption of the quartz plate is much less than 30 per cent.*

* At first sight the explanation of these results might appear to lie in a possible shifting of the " 2.8μ band" towards the shorter wave-length with rise of temperature and towards the greater wave-lengths as the temperature decreases. Such an explanation, however, would involve a shifting to an extent which is scarcely probable—from say about 1μ at 2400°C. abs. to about 4μ at 1000°C. abs. Some interesting possible explanations may be inferred from the following facts discovered by Coblenz:—(i) The absorption spectrum of water vapour shows a strong band (or series of bands) extending from about 4μ to about 8μ ; (ii) the absorption spectrum of oxygen (of which there is a little in the exploded mixtures) shows shallow bands whose maxima are at 3.2μ and 4.7μ ; and (iii) nitrogen (of which there is, of course, a large amount in the exploded mixtures) gives a strong emission band in a vacuum tube whose maximum is at 1μ approximately.

PART II.—INTRINSIC RADIANCE AND TRANSPARENCY MEASUREMENTS.

The curves in fig. 4 show the rate of emission of radiation from unit solid angle (*i.e.*, the intrinsic radiance) of 25·4 per cent. hydrogen mixtures at various gas temperatures. Curve A gives the intrinsic radiance of the

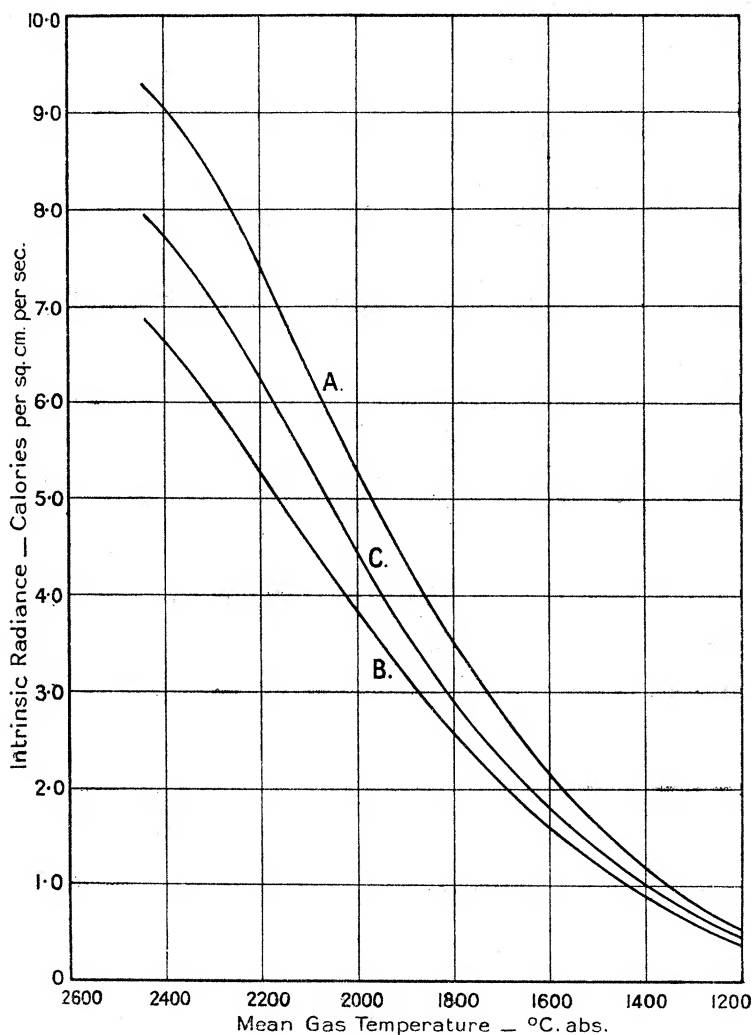


FIG. 4.

mixture when contained in the vessel with its silver-plated walls polished. Curve B gives the intrinsic radiance of the mixture when the walls of the vessel were blackened; and curve C gives similar information in respect to a mixture of the same composition contained in the blackened vessel with a polished circular patch (about 6 inches in diameter) on the end-cover opposite

the bolometer. By this means the cone of gas from which the radiation is measured is reflected back upon itself and its virtual length is thus 60 cm. (*i.e.*, double the length of the vessel), or rather from a virtual thickness of 59 cm. allowing from 2 to 3 per cent. for the absorption of the silver-plating.

From curves A and B (fig. 4) it will be seen that the hydrogen mixture in the polished vessel emits about 35 per cent. more strongly than in the blackened vessel—the emission being compared in the two cases at the same mean gas temperature. Coal-gas mixtures under similar conditions emitted about 65 per cent. more strongly in the polished vessel than in the black vessel in the initial stages of cooling and about 50 per cent. more strongly after the gas temperature had fallen to about 1600° C. abs.* When discussing the coal-gas results it was pointed out that they were probably due to the vibratory energy of the radiating molecules and the transparency of the gaseous mixture being greater in the polished vessel than in the black vessel, and it is probable that similar causes are responsible for the hydrogen results.

An indication of the transparency of the hydrogen mixtures in the black vessel to radiation of the same kind as they emit may be obtained by comparing the intrinsic radiance from 59 cm. (curve C) with that from 30 cm. (curve B). This comparison is made in Table VIII and a similar comparison for coal-gas mixtures is added. It will be seen that the intrinsic radiance from 59 cm. is about 15 per cent. greater than that from 30 cm. in the early stages of cooling and drops to about 10 per cent. after the gas temperature has fallen to about 1600° C. abs. The ratios for the coal-gas mixtures show that they are much more transparent in the early stages of cooling and much less transparent after the temperature has fallen to below 1600° C. abs. than the hydrogen mixtures.

Table VIII.

Mean gas temperature (° C. abs.).	Intrinsic radiance from 59 cm. in vessel with black walls Intrinsic radiance from 30 cm. in vessel with black walls	
	25·4 per cent. hydrogen mixtures.	15 per cent. coal-gas mixtures.
2430	1·15	1·27
2400	1·15	1·25
2200	1·17	1·2
2000	1·17	1·14
1800	1·12	1·1
1600	1·1	1·08
1400	1·1	1·0 (nearly)
1200	1·1	1·0

* 'Phil. Trans.,' A, vol. 211, p. 397, Table XII.

Prof. Callendar experimenting with Meker burner flames has shown that the exponential law of absorption is closely obeyed in flame,* and following him I have shown that it is closely obeyed in exploded coal-gas mixtures contained in a closed vessel.† Assuming this law to hold for the hydrogen mixtures the coefficient of absorption has been calculated from intrinsic radiance measurements for 59 cm. and 30 cm. in the black vessel and tabulated in Table IX. The intrinsic radiance from an infinite thickness of the gaseous mixture (which in this case is the intrinsic radiance from a blackened cylindrical vessel of 30 cm. diameter and of very great length) has also been added. This has been calculated from the formula

$$R_{ix} = R_{i\infty} (1 - e^{-Kx})$$

where R_{ix} is the intrinsic radiance from x cm. of gas,‡

$R_{i\infty}$ is the intrinsic radiance from an infinite thickness and

K is the coefficient of absorption per cm.

Table IX.

Mean gas temperature (° C. abs.).	Intrinsic radiance in black vessel (cals. per sec.).			Coefficient of absorption, K .
	From 30 cm. (observed).	From 59 cm. (observed).	From infinite thickness (calculated).	
2440	6·9	7·95	8·1	0·062
2400	6·7	7·75	7·9	0·062
2200	5·3	6·2	6·4	0·06
2000	3·8	4·45	4·55	0·06
1800	2·6	2·9	2·95	0·72
1600	1·6	1·8	1·85	0·75

SUMMARY OF RESULTS.

The following are the main results obtained from these experiments:—

Part I.—When mixtures of hydrogen and air of various strengths at atmospheric density are exploded in the vessel when its walls are coated with a thin layer of dull black paint—

(i) the proportion of the heat of combustion lost by radiation during explosion and subsequent cooling decreases greatly with the mixture strength (see Table IV).

* ‘Third Report of British Association Committee on Gaseous Explosions,’ Appendix I.

† ‘Phil. Trans.,’ A, vol. 211, p. 401.

‡ As R_{ix} varies with the lateral dimensions as well as with the thickness, x , this formula only holds good for the gaseous mixture in a blackened cylindrical vessel of 30 cm. diameter and of varying length or thickness.

(ii) The total radiation emitted during explosion and subsequent cooling is a linear function of the maximum absolute temperature developed (see p. 187).

(iii) The proportion of the heat of combustion lost by radiation up to the moment of maximum temperature varied between 0·5 per cent. (for the strongest mixture experimented upon) and 1·4 per cent. (for the weakest mixture) (see Table V).

(iv) The maximum rate at which radiation is emitted occurs approximately at the point at which the temperature developed is a maximum (see p. 191).

(v) Weak mixtures radiate more powerfully in the initial stages of cooling than stronger mixtures when they have cooled to the same mean temperatures as the weaker mixtures have in this epoch (see fig. 5).

(vi) The rate of emission of radiation in the strongest mixture is approximately proportional to the fourth power of the absolute temperature of the gaseous mixture. This proportionality does not hold in the initial stages of cooling of the weak mixtures, but it holds satisfactorily in the later stages of cooling (see fig. 5).

(vii) The $2\cdot8\mu$ emission band of steam (hydrogen flame) ceases to be emitted in the hydrogen mixtures when the gas temperature has fallen to about 1000° C. abs. It would appear radiation of greater wave-length is emitted which contains appreciable energy at this temperature. At the highest temperatures in the 25·4 per cent. mixtures radiation of shorter wave-length than $2\cdot8\mu$ would appear to be emitted (see p. 192).

Part II.—The following results refer to experiments made in the vessel whose walls were silver-plated and therefore could be made either reflecting or absorbent as regards radiation—

(viii) The intrinsic radiance at any given temperature after explosion increases greatly as the reflecting power of the interior surface of the explosion vessel is increased; in other words, the intrinsic radiance at any given temperature increases with the size of the vessel (see p. 194).

(ix) The gaseous mixtures after explosion are very transparent throughout cooling to radiation of the same kind as they emit.

DISCUSSION OF RESULTS.

In discussing the results of the coal-gas and air experiments, it was pointed out that the energy in the vibratory degrees of freedom which gives rises to infra-red radiation appeared to be dependent upon density and volume as well as upon temperature.* The hydrogen experiments made in the reflecting vessel lend further support to the view that the vibratory energy is

* 'Phil. Trans.,' A, vol. 211, p. 410.

dependent upon volume as well as upon temperature. The effect of density in these mixtures was not investigated.

The experiments indicate that radiation phenomena in hydrogen mixtures are in general similar to those in coal-gas mixtures. In one or two respects, however, they show important differences, and these will here be briefly discussed.

As has been pointed out, the most noticeable difference lies in the fact that the rate of emission was not found to be a maximum during the explosion period, as was found to be the case in the coal-gas mixtures. That the rate of emission in the latter mixtures was greater during the explosion period (when the bulk of the chemical combination takes place) than at the moment of maximum temperature (when the bulk of chemical combination has been completed) was taken to support the theory that the energy of combination first passes (either wholly or in part) into the form of intramolecular energy, which is afterwards partitioned off in part into translational energy.* The hydrogen experiments do not appear to support this theory. A possible explanation is that combination between hydrogen and oxygen molecules is a simple transaction and may be completed within a time which might suitably be measured by molecular standards, whereas the combustion of hydrocarbon molecules may be a long-drawn-out process, which takes an appreciable time. In the light of this suggestion, it is clear that the volume of the hydrogen mixtures undergoing combination at any instant would be an infinitesimal fraction of the whole even during the period of greatest chemical activity, and consequently the influence of chemical activity on the radiation emitted (which comes from the whole mass of the gaseous mixture) would not be detected.

In another important respect do the hydrogen mixtures differ from the coal-gas mixtures. The proportion of the heat of combustion lost by radiation during explosion and subsequent cooling decreases with the mixture strength (and therefore with the maximum temperature developed) much more rapidly in the hydrogen mixtures than in the coal-gas mixtures. The explanation of this is pretty clear in the light of some experiments on the analysis of the radiation emitted in coal-gas and hydrogen mixtures.† The exploded weak hydrogen mixtures spend only a comparatively short period of their radiating history at temperatures at which they emit the 2.8μ band (in which is concentrated the bulk of the radiation energy in these mixtures). The weak coal-gas mixtures, on the other hand, spend a considerable proportion of their

* 'Phil. Trans.,' A, vol. 211, p. 410.

† 'Phil. Mag.,' January, pp. 84-95 (1920).

history at radiating temperatures, both on account of their much slower cooling and also because they emit the strong $4.4\ \mu$ band of CO_2 , which continues to be emitted at temperatures at which the $2.8\ \mu$ band ceases to be emitted.

The experiments of Holborn and Henning on the specific heat of gases, although probably subject to a systematic error, as pointed out by Prof. Callendar,* show quite certainly that the rate of increase of the specific heat of steam increases very considerably with the temperature. Thus, over the temperature interval $100^\circ\text{C}.$ – $600^\circ\text{C}.$ it increases by about 4 per cent., while over the interval $600^\circ\text{C}.$ – $1100^\circ\text{C}.$ it increases by as much as 24 per cent. The quartz experiments would appear to throw some light on this. The emission spectrum of steam (hydrogen flame) consists essentially of a strong band at $2.8\ \mu$, and these experiments indicate that the energy in the vibratory degrees of freedom corresponding to radiation of this wave-length is not appreciable at temperatures below $700^\circ\text{C}.$ ($1000^\circ\text{C}.$ abs.), but above this temperature these degrees begin to share to a rapidly increasing extent in the heat motion of the molecules.

The experiments described in this paper were all made in the Engineering Laboratory at Cambridge in the years previous to the war. The laboratory was then under the control of the late Prof. B. Hopkinson, and I desire to place on record my great indebtedness to him for the valuable advice and assistance he so readily gave me.

* Appendix to 'First Report of British Association Committee on Gaseous Explosions.'
